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The Influence of the Precursor's Deposition Order on the Properties of CZTSe Thin Films

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Abstract. $Cu_2ZnSnSe_4$ (CZTSe) polycrystalline thin films have been prepared on molybdenum coated soda-lime glass substrates by DC magnetron sputtering technique. Two different deposition orders for the metallic precursors were tested, namely Mo/Cu/Zn/Sn and Mo/Zn/Cu/Sn. The influence of the precursor's deposition order on the structural and optical parameters of the obtained thin films was studied. Structural analyses were done based on the results of XRD and stylus profilometry measurements. Optical transmittance measurements were performed in order to estimate the band gap energy of the CZTSe films. All XRD spectra show preferred growth orientation along (112) crystallographic plane. The average size of the grains calculated from XRD data is slightly bigger for the Mo/Zn/Sn/Cu sequence. The profilometry analysis shows that the average roughness and thickness of the layer were also bigger for that deposition order. Optical band gap energies derived from transmittance measurements were 1.23eV and 1.27eV for Mo/Cu/Zn/Sn and Mo/Zn/Cu/Sn, respectively.

Keywords: $Cu_2ZnSnSe_4$, thin film solar cell, DC magnetron sputtering, selenization, XRD

1. Introduction

$Cu(In,Ga)(S,Se)_2$ (CIGS) based solar cells with efficiencies of up to 19.9% [1] need expensive and rare materials such as In and Ga, which influences the cost of these modules and thus hinders their large-scale production [2]. In order to produce cost-effective photovoltaic cells, alternative low-cost chalcopyrite-like semiconductors such as Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) have been studied since 1997 [3].These materials have been considered as one of the most promising absorber layer materials due to their direct band gap with the value of $1.0-1.5eV$ (depending on the composition), which is close to the optimum value for a single junction solar cell, high absorption coefficient and p-type electrical conductivity [4, 5]. The maximum achieved device efficiencies for CZTSSe and CZTSe solar cells were 12.6% [6] and 11.6% [7], respectively.

CZTSe thin films can be prepared by various techniques such as thermal evaporation [8], chemical vapor deposition [9], sputtering [10], electrochemical deposition [11], sol-gel method [12] etc. Among these techniques, vacuum growth techniques have advantages of scalability and controllability [13]. However, there is no general agreement on which one is optimal for the fabrication of CZTSe films.

In this paper, DC magnetron sputtering in an argon (Ar) atmosphere was used to prepare CZT thin films on soda lime glass (SLG) substrate coated with molybdenum (Mo), which serves as the back contact for the final solar cell and was chosen due to its suitable thermal, mechanical and electrical properties [14, 15]. Afterwards, samples were selenized at 450^0C in order to obtain CZTSe thin films. The difference between the samples was the order of metallic precursors deposition, namely the sequences of the sputtering were Mo/Cu/Zn/Sn/Se and Mo/Zn/Cu/Sn/Se for the first and second sets, respectively. The effect of the Cu precursor's deposition order on CZTS thin film properties was previously described by Fernandes *et al.* [16, 17].The effect of the precursor's order on the structural and optical properties of CZTSe thin films (such as the formed phases present in the compound), average grain size, layer thickness and average roughness of the surface was studied.

2. Experimental details

CZTSe thin films were prepared by a two-step method. In the first step, Mo back contact was deposited on the cleaned $1\times1cm^2$ SLG substrate by DC magnetron sputtering. The deposition of Mo layer was performed under the following conditions: base pressure -10^{-3} mbar, working pressure $-8\cdot10^{-2}$ mbar, deposition time and working current – 20 minutes with $0.4\dot{A}$ and 80 minutes with 0.6A sequentially. Then, Cu, Zn and Sn metallic precursors with 99.999% purities were sputtered on the prepared substrate by the same method. Targets were positioned at 10 cm distance from the substrate during the whole process. The sputtering conditions for the individual precursors were the followings: 7 minutes at $8\cdot10^{-2}$ mbar operating pressure with 0.2 A working current, 5 minutes at $7\cdot10^{-2}$ mbar pressure with 0.3 A working current and 20 minutes at $7\cdot10^{-2}$ mbar pressure with 0.3 A working current for Cu, Zn and Sn, respectively. This procedure was repeated 3 times. The deposition conditions were chosen to yield a film having a nominal thickness of about 600 nm. All depositions were performed under Ar atmosphere as it was mentioned before. Two variations of the precursor's deposition order were tested, namely Mo/Cu/Zn/Sn and Mo/Zn/Cu/Sn (the sequence variable was the Cu position). For the second step, a special graphite container with different compartments for pure Se and already prepared SLG/Mo/CZT samples was used for the selenization process. The container was loaded into a quartz tube, evacuated by a mechanical pump (base pressure of 10^{-2} mbar) and heated. The selenization process itself consists of three thermal steps. At first, the samples were kept in 120^0C for 10 minutes. Then they were heated up to 200^0C and kept at that temperature for 20 minutes. Finally, the samples were kept at 450^0C temperature for 30 minutes for the formation of the $Cu_2ZnSnSe_4$ phase.

Structural properties of the obtained thin films were analyzed by X-ray diffraction (XRD) spectroscopy with CuK_α ($\lambda=1.5404\,\mathring{A}$) monochromatic source. Surface properties were measured by a Mitutoyo surftest SJ-410 profilometer. Optical transmittance measurements were taken by a SF-26 LOMO spectrophotometer.

3. Results and discussion

Figure 1 shows the XRD patterns of CZTSe thin films selenized at $450^0 C$. The obvious peaks could be attributed to the (112), (220/204) and (312/116) crystallographic orientations, and the (400/008) and (312/116) doublet peaks may refer to a tetragonal stannite structure of the obtained films [18]. The sharpness of the major peaks indicates a good crystallinity. The strongest peak for all samples occurred in the (112) direction at $2\theta = 27.14^0$. In general, all the patterns are similar and the main difference between XRD patterns of samples with different deposition orders of precursors was the appearance of a peak along the (200) plane for the Mo/Zn/Cu/Sn samples. In order to determine whether the CZTSe grains have a preferential orientation, in which grains were crystallized, we have calculated the texture coefficient for the above-mentioned three strongest peaks by the following equation [19]:

$$TC(hkl) = \frac{\frac{I_{nw}(hkl)}{I_0(hkl)}}{\frac{1}{N}\sum_{1}^{N}\frac{I_{nw}(hkl)}{I_0(hkl)}},$$

where $I_{nw}(hkl)$ and $I_0(hkl)$ are the measured and standard integrated intensities for given (hkl) reflection respectively, and N is the number of peaks (we took $N = 3$). The calculated TCs are shown in figure 2. The (112)-oriented grains are clearly textured, since TC is more than 1 for all samples (TC>1 indicates preferential orientation [19]). All the remaining TC values are less than 1, which means that $Cu_2ZnSnSe_4$ grains have a preferred orientation perpendicular to a (112) crystallographic direction at $2\theta = 27.14^0$.

No secondary phases (i.e. CuSe, $CuSe_2$) were detected on the diffraction patterns. The calculated lattice parameters are $a = 5.681\,\text{Å}, c = 11.353\,\text{Å}$, and $\frac{c}{a} = 1.998$, which is in good agreement with the known data [20, 21]. The average crystallite size for the CZTSe polycrystalline layer was also calculated using the $L = \frac{K\lambda}{B\cos\theta}$ Scherrer equation [22], where $K = 0.94$ is the dimensionless shape factor or Scherrer constant, B is the line broadening at half of the intensity maximum (FWHM in radians), θ is the Bragg angle and λ is the X-ray wavelength ($1.5404\,\text{Å}$). The results of calculations for all samples are presented in Table1. It is noticeable that the grains are slightly larger for Mo/Zn/Cu/Sn samples and equal to 300 nm, which is large enough for usage in thin film based solar cells as the absorber layer (large grains increase the conversion efficiency of polycrystalline solar cells [23]).

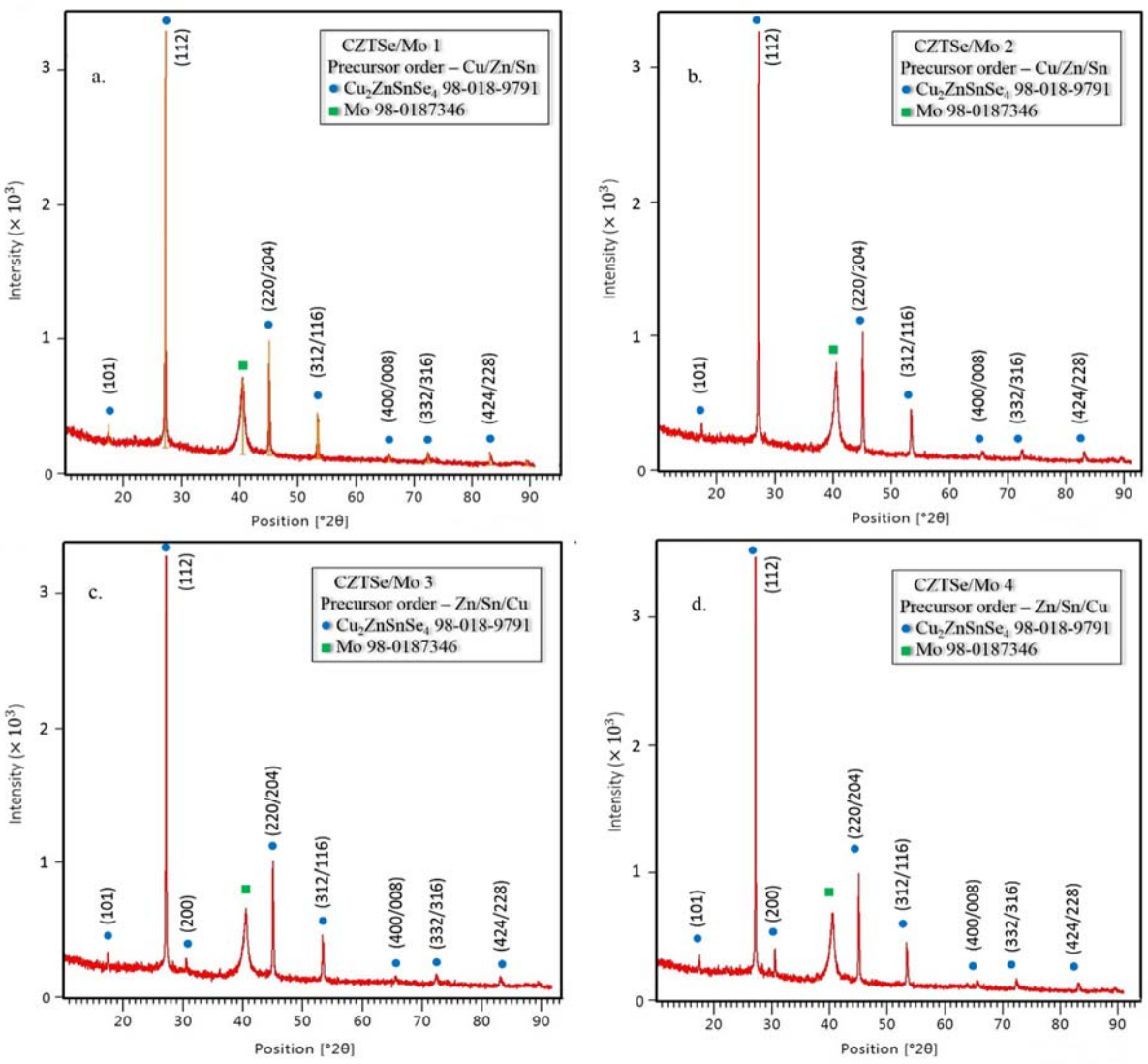

Fig. 1. XRD spectra of the samples with precursor's deposition order of *a, b*)-Mo/Cu/Zn/Sn and *c, d*)-Mo/Zn/Sn/Cu.

Results of the measurements of the grown layer thicknesses and average roughness are presented in figure 3. It is observable, that both thickness and roughness have identical values for the two chosen precursor sequences. The difference appears after the selenization process, which can be explained by the formation of other phases on the surface of the layer, which were not detected by XRD or coincided with the CZTSe peaks.

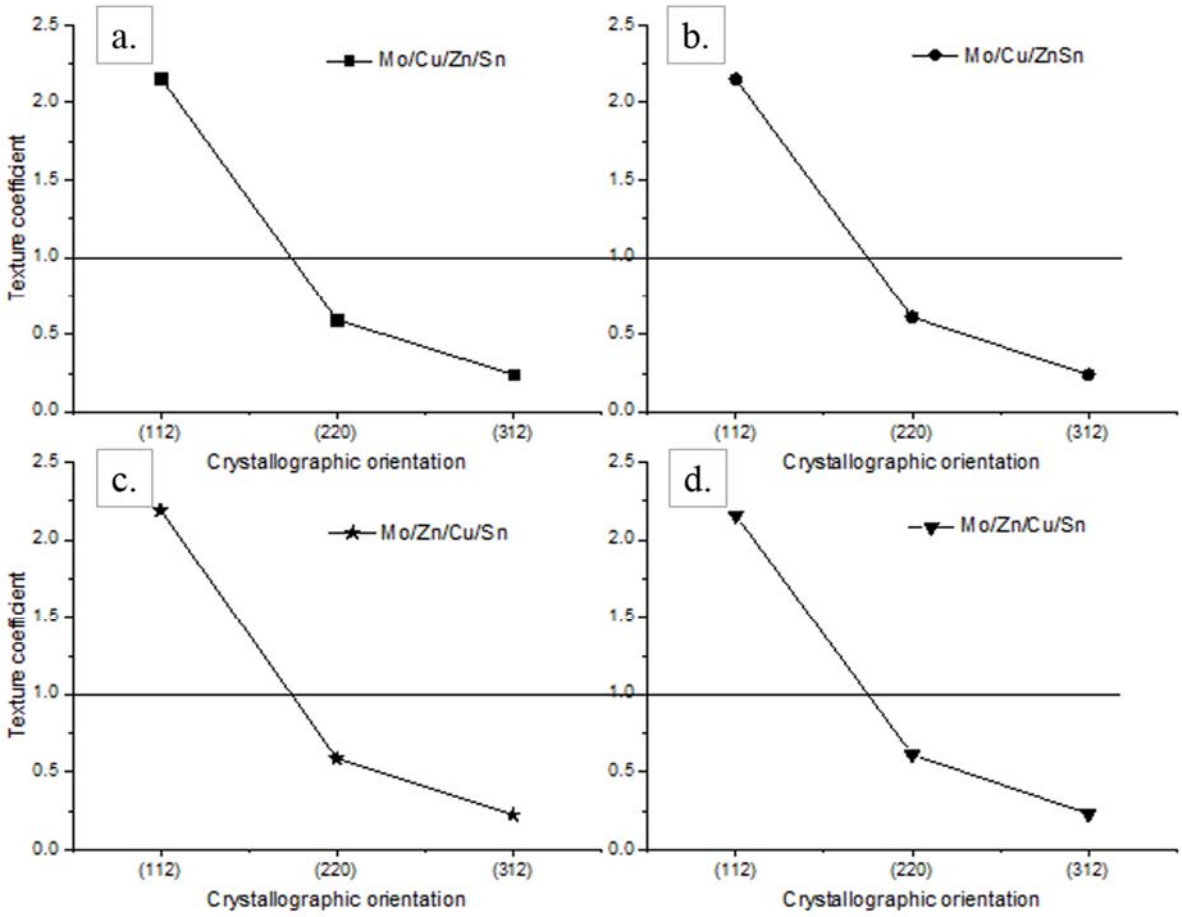

Fig. 2. Texture coefficients of the (112), (220) and (312) reflections of the CZTSe films.

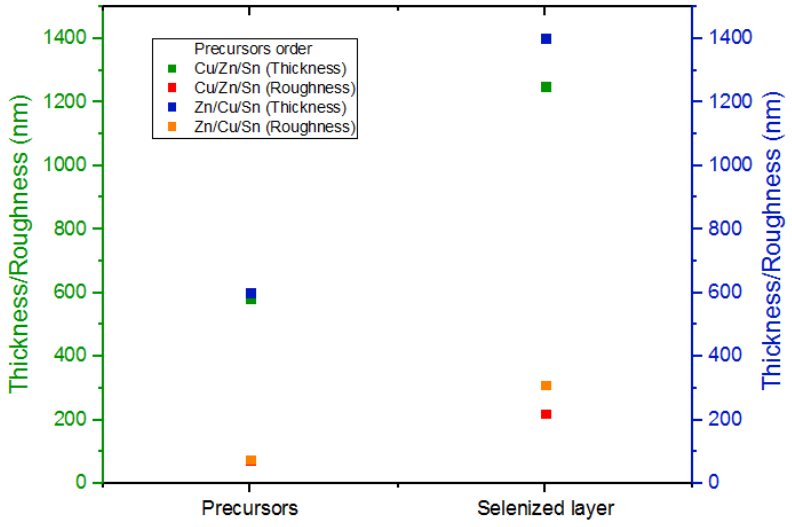

Fig. 3. The thickness and average crystallite size of CZTSe films before and after selenization.

Table 1. The summarized properties of CZTSe thin films grown with different sequences of the precursor.

Samples	Average crystallite size (nm)	Layer thickness (nm) Precursor/Selenized	Average roughness (nm) Precursor/Selenized	Optical band gap (eV)
a,b (Mo/Cu/Zn/Sn)	285	580/1250	72/220	1.23
c, d (Mo/Zn/Cu/Sn)	300	600/1400	75/310	1.27

The optical properties of CZTSe thin films were studied through optical transmission measurements and the results are presented in figure 4. The graphs show a slight increase of the slope of the curve for the Mo/Zn/Cu/Se precursor's order. Therefore, a better-defined absorption edge is obtained. The optical absorption coefficient was calculated using the relation $\alpha = -\ln(T)/d$, where T is a transmittance value and d is the thickness of the layer [24]. All investigated samples have a large absorption coefficient in the order of $10^4 cm^{-1}$ near a fundamental absorption edge. In order to calculate band gap energies, $(\alpha h\nu)^2$ vs $(h\nu)$ plots were built (figure 5), where h is a Plank's constant and ν is a frequency of the vibration. The band gap energy was calculated by the widely used Tauc plot method [25] according to which $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where A is a proportional constant and the value of n indicates the type of transition (in our case $n = 1/2$ or direct allowed transition). The estimation of the band gap energy was done by extrapolating the tangent line of the absorbance to the horizontal axis. The optical band gap value for the sample with precursor's order of Mo/Zn/Cu/Sn was slightly bigger than that of the Mo/Cu/Zn/Sn sample due to above described absorption edge differences.

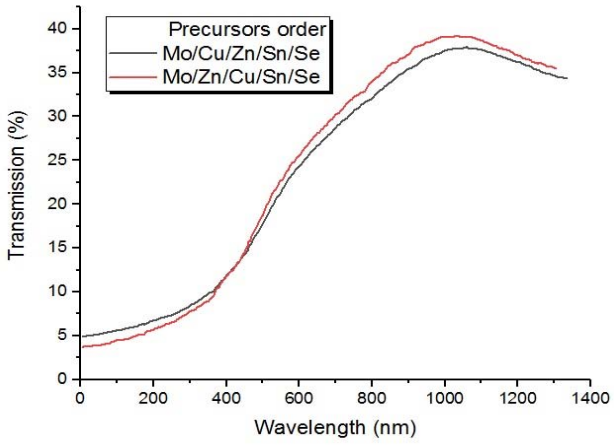

Fig. 4. Optical transmittance results for the two types of the precursor's deposition order.

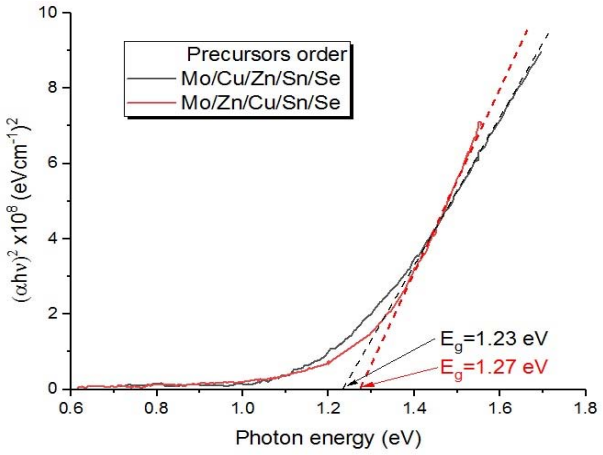

Fig. 5. $(\alpha h\nu)^2$ vs photon energy of CZTSe thin films.

4. Conclusions

Thus, we have prepared CZTSe thin films on Mo-coated SLG substrates by DC magnetron sputtering with different sequences of metallic precursors in order to clarify the influence of the precursor's deposition order on the properties of the films. XRD patterns of the CZTSe thin films show that they have a tetragonal stannite-type structure with preferred orientation of the growth along the (112) crystallographic direction. No secondary phases were detected on XRD spectra of the samples. The

samples with Mo/Zn/Cu/Sn sequence have an additional peak at $2\theta = 30.5^0$ (perpendicular to (200) plane). The more significant difference for different sequences appears in the measurements of the layer thickness and average roughness. Namely, after the selenization process both thickness and roughness were bigger for the Mo/Zn/Cu/Sn samples. The optical bandgap energy values of the investigated samples were 1.23eV and 1.27eV for Mo/Cu/Zn/Sn/Se and Mo/Zn/Cu/Sn/Se, respectively. Therefore, to a first approximation, more suitable properties for fabrication of high efficiency solar cells were obtained for CZTSe thin films with the Mo/Zn/Cu/Sn precursor's order.

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